Metallacycle Transfer from Zirconium to Main Group Elements: A Versatile Synthesis of Heterocycles

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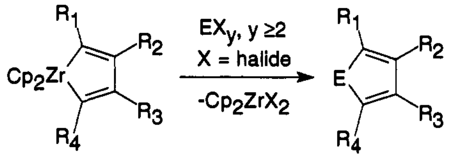
Abstract: The reaction of zirconium metallacycles is used to produce a variety of main group heterocycles including borole Diels–Alder dimers, galloles, indacyclopentadienes, siloles, germoles, stannoles, phospholes, arsoles, stiboles, bismoles, thiophenes, selenophenes, dihydrothiophenes, dihydroselenophenes, tetrahydrothiophenes, tetrahydroselenophenes, stannacyclopentanes, phospholenes, and isothiazoles. An X-ray crytallographic study of the borole Diels–Alder dimer of 1-phenyl-2,3,4,5-tetramethylborole is discussed and compared with the structure of 7-norbornenyl carbenium ions. The scope and potential for this metallacycle transfer reaction are delineated.

Introduction

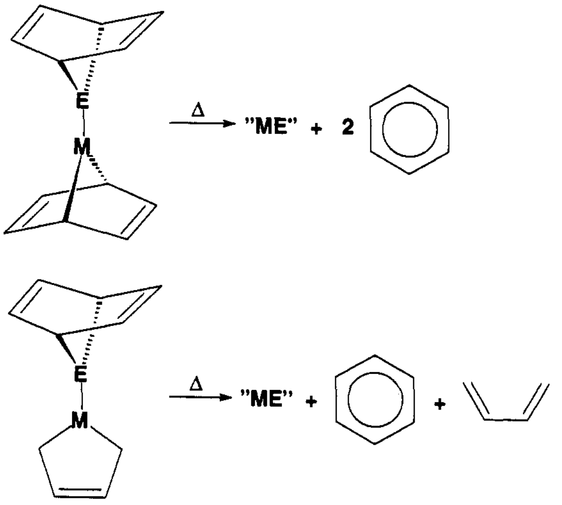
Heterocyclic compounds have long played a dominant role in medicinal chemistry and in the science of crop protection.[1] More recently, heterocycles have received increasing attention in the field of material science.[2] Several years ago we described[3] a new and general synthetic route which provides access to main group heteroles via "metallacycle transfer" of a carbon fragment from a readily available zirconacyclopentadiene to a main group halide (for example, eq 1). Others have subsequently extended the scope of this chemistry so that this type of transformation now provides a broadly useful synthetic route to heteroles and other heterocycles of the group 13–16 elements.[4–7]



(1)

Our development of this chemistry grew from an interest in main group elementanorbornadiene compounds of the type shown in Scheme 1. These compounds might be precursors for the synthesis of thin films of solid materials by cheletropic elimination of arenes or dienes at higher temperatures. It was envisioned that the most efficient route to these types of compounds would be through Diels-Alder addition of acetylenes to the elementacyclopentadiene compounds. The preparations of the latter compounds in the literature, however, were typified in general by low yields and difficult procedures.[8] Alternative synthetic routes were sought and, as we communicated previously,[3] the metallacycle transfer approach embodied in eq 1 proved advantageous.

Scheme 1



One noteworthy application of eq 1 has been the synthesis of borole derivatives.[9] The chemistry of the borole ring system A has not been extensively studied owing to a lack of synthetic routes to this species attendant with its high reactivity.[10] The only known stable monomeric borole that has been reported is pentaphenylborole.[10–12] Metallacycle transfer from zirconium to boron[13] provided a route to Diels–Alder dimers of the borole ring system, of which only one was known previously.[14] We were

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[†] Contribution No. 6661.

[●] Abstract published in *Advance ACS Abstracts*, February 15, 1994.

(1) Taylor, E. C., Ed. *The Chemistry of Heterocyclic Compounds:* Wiley: New York, 1993.

(2) See, for example: Wong, C. P., Ed. *Polymers for Electronic and Photonic Applications*; Academic: Boston, MA, 1993; pp 1–661.

(3) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310–12.

(4) Group 14 elements: (a) Dufour, P.; Dubac, J.; Dartiguenave, Y. *Organometallics* **1990**, *9*, 3001–3. (b) Dufour, P.; Dartiguenave, M.; Dartiguenave, Y.; Dubac, J. *J. Organomet. Chem.* **1990**, *384*, 61–9. (c) Meier-Brocks, F.; Weiss, E. *J. Organomet. Chem.* **1993**, *453*, 33.

(5) Group 15 elements: (a) Douglas, T.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*. 1367–8. (b) Buchwald, S. L.; Fisher, R. A.; Foxman, R, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*. 771–2. (c) Schenk, W. A.; Voss, E. *J. Organomet. Chem.* **1990**, *396*, C8–C11. (d) Sendlinger, S. C.; Haggarty, B. S.; Rheingold, A. L.; Theopold, K. H. *Chem. Ber.* **1991**, *124*. 372–4. (e) Ashe, A. J.; Kampf, J. W.; Altaweel, S. M. *J. Am. Chem. Soc.* **1992**, *114*, 372–4. (f) Ashe, A. J.; Kampf, J. W.; Altaweel, S. M. *Organometallics* **1992**, *11*, 1491–6. (g) Spence, R. E. V.; Hsu, D. P.; Buchwald, S. L. *Organometallics* **1992**, *11*, 3492–3.

(6) Group 16 elements: (a) Buchwald, S. L.; Qun, F. *J. Org. Chem.* **1989**, *54*. 2793–7. (b) Tour, J. M.; Wu, R. L.; Schumm, J. S. *J. Am. Chem. Soc.* **1990**, *112*. 5662–3. (c) Cuny, G. D.; Gutierrez, A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 537–9. (d) Mohamadi, F.; Spees, M. M. *Organometallics* **1992**, *11*. 1398–1400.

(7) For extensions to the synthesis of four-membered-ring heterocycles including 1,2-dihydrophosphetes, see: Doxsee, K. M.; Shen, G. S.; Knobler, C. B. *J. Am. Chem. Soc.* **1989**, *111*, 9129–30. Tumas, W.; Suriano, J. A.; Harlow, R. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29* , 75–6. Doxsee, K. M.; Hanawalt, E. M.; Shen, G. S.; Weakly, T. J. R.; Hope, H.; Knobler, C. B. *Inorg Chem.* **1991**, *30* , 3381–9.

(8) For recent reviews on synthetic routes to group 14 and 15 heteroles, see: (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215–63. (b) Mathey, F. *Chem. Rev.* **1988**, *88*, 429–53 (c) Mathey, F. *Rev. Heteroat. Chem.* **1992**, *6*, 1–24.

(9) Fagan, P. J.; Burns, E. G.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*. 2979–81.

(10) (a) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*. 379–85. (b) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436–7. (c) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1977**, *127*. C9–C13. (d) See also: Killian, L.; Wrackmeyer, B. *J. Organomet. Chem.* **1978**, *148*, 137–46. (e) Schacht, W.; Kaufmann, D. *Angew. Chem.* **1987**, *99*. 682–3.

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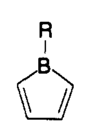
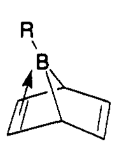


A



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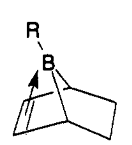


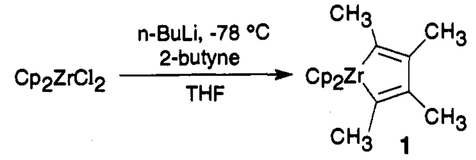
C

able to demonstrate that these dimers could be cracked in situ to the monomeric boroles. These act as prolific dienes in Diels–Alder reactions with unactivated alkenes and acetylenes to produce boranorbornadiene and boranorbornene systems **B** and **C**.[15] Structurally, the Diels–Alder dimers were found to contain a two-electron three-centered bond between a boron and a carbon–carbon double bond.[9] This bonding is isoelectronic with that originally proposed for 7-norbornenyl carbenium ions.[16] Subsequent to our report, a 7-norbornenyl cation was crystallographically characterized by Laube.[17] A strong structural resemblance between the 7-boranorbornadiene structural unit and the 7-norbornenyl cation was observed, a point which is further discussed in this paper.

Perhaps the most remarkable feature of the metallacycle transfer reaction is its generality. Variation of EX_y (E = main group moiety) in eq 1 has allowed us to synthesize heterole derivatives of a dozen different main group elements. Here we provide experimental details for the syntheses of the heteroles we have prepared via eq 1. In addition, we have significantly expanded this chemistry to allow the synthesis of 2,3-dihydroheteroles, 2,4-dihydroheteroles, tetrahydroheteroles, and even ring systems such as isothiazoles which incorporate two different heteroatoms in the ring.[18]

Results

A. Elementacyclopentadienes: Phospholes, Arsoles, Stiboles, Bismoles, Siloles, Germoles, Stannoles, Galloles, and Indacyclopentadienes. Zirconacyclopentadiene **1** was synthesized in high yield by the reduction of zirconocene dichloride in the presence of 2-butyne (eq 2), a method first reported by Negishi and coworkers.[19] Zirconacycle **1** can be isolated as a red-orange crystalline solid.[20] This metallacycle is soluble in THF and toluene but only slightly soluble in hexane. Similarly, the zirconium metallacycle **2** was prepared from 2,8-decadiyne[21] and isolated. However, the zirconacycles need not be isolated. For example, the known compound **3**[22] was generated from diphenylacetylene and used in situ. Treatment of **1** with 1 equiv of dichlorophenylphosphine or -arsine in THF results in an immediate reaction according to eq 3. The products 1-phenyl-2,3,4,5-tetramethylphosphole (**4a**) and 1-phenyl-2,3,4,5-tetramethylarsole (**4b**) could be readily isolated by either flash chromatography or distillation in 81% and 78% yield, respectively.[23,24] The analogous stibole and bismole can be prepared by first treating **1** with $SbCl_3$ or $BiCl_3$ to make the corresponding 1-chloro-2,3,4,5-tetramethylstibole and -bismole. These compounds are thermally unstable and were therefore treated in situ with 1 equiv of phenyllithium, affording **4c** and **4d**, respectively. Compound **4c** was isolated as a liquid after flash chromatography in 78% yield, and **4d** was obtained as a crystalline solid by sublimation in 70% yield.



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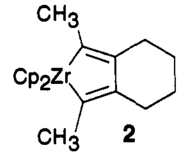

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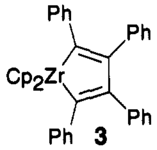

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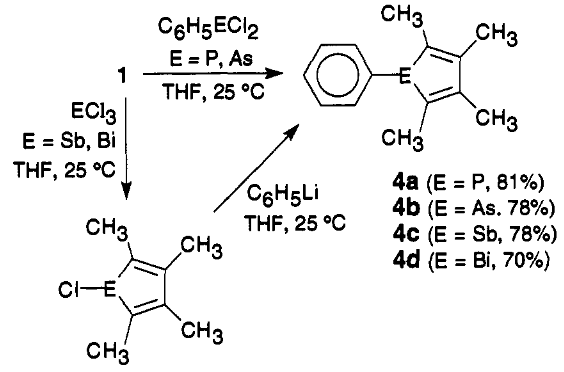

(3)

The reaction of **1** with group 14 elements similarly produced siloles, germoles, and stannoles. The reaction of **1** with silicon halides produced siloles only with difficulty. Indeed, **1** can be recovered unchanged after heating in *neat* $SiCl_4$. Assuming bromide would be a better leaving group, the metallacycle **1** was treated with neat $SiBr_4$ for 2 days at 150 °C, after which time the red color of **1** had dissipated. Subsequent workup did yield silole **5a** as an impure liquid in ca. 28% yield (eq 4). We did not attempt to optimize this reaction further or try silicon reagents with better leaving groups. The reaction of **1** with $GeCl_4$ proceeded quite readily at room temperature, and the germole **5b** could be isolated in 83% yield as a volatile crystalline solid. Using metallacycle **2**, the stannole **6** could be produced in good yield after reaction with $(CH_3)_2SnBr_2$ (eq 5).

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[11] The coordination and stabilization of the borole ring system with transition metals has been well documented: (a) Siebert, W. *Angew. Chem.* **1985**, *97*, 924–39. (b) Herberich, G. E.; Carstensen, T.; Englert, U. *Chem. Ber.* **1992**, *125*, 2351-7 (the nineteenth of a series of papers on metal borole derivatives).

[12] Boroles with annulated arene rings are known, but the chemistry of such compounds differs substantially from the parent ring systems.

[13] For examples of transfer of acyclic carbon fragments from zirconium to boron, see: (a) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2361. (b) Fryzuk, M. D.; Bates, G. S.; Stone, C. *J. Org. Chem.* **1988**, *53*. 4425–6 (c) Cole, T. E.; Quintanilla, R.; Rodewald, S. *Organometallics* **1991**, *10*. 3777–81.

[14] (a) Herberich, G. E.; Ohst, H. *Chem. Ber.* **1985**, *118*. 4303–13. (b) Herberich, G. E.; Buller, B.; Hessner, B.; Oschmann, J. *J. Organomet. Chem.* **1980**, *195*. 253–9.

[15] Details of the Diels–Alder chemistry of boroles will be given elsewhere. See ref 9. Fagan, P. J.; Burns, E.; Petrovich, L.; Calabrese, J. C. To be submitted for publication.

[16] Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 6803–6, and references therein.

[17] Laube, T. *J. Am. Chem. Soc.* **1989**, *111*, 9224–32.

[18] For a related approach to benzo-fused heterocycles containing two different heteroatoms, see: (a) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*. 7137–41. (b) Buchwald, S. L.; Fisher, R. A.; Davis, W. M. *Organometallics* **1989**, *8*. 2082–4. (c) Fisher, R. A.; Nielsen, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*. 165–71.

[19] (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829–32. (b) Swanson, D. R.; Negishi, E. *Organometallics* **1991**, *10*, 825–6.

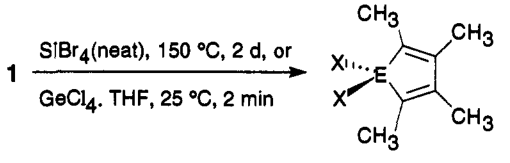
[20] Zirconacycle **1** can also be prepared using amalgamated magnesium turnings as the reductant: Thanedar, S.; Farona, M. F. *J. Organomet. Chem.* **1982**, *235*, 65–8.

[21] Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788–96.

[22] (a) Hunter, W. E.; Atwood, J. L.; Fachinetti, G.; Floriani, C. *J. Organomet. Chem.* **1981**, *204*, 67–74. (b) Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.*, **1977**, *132*, 223. (c) Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 5936.

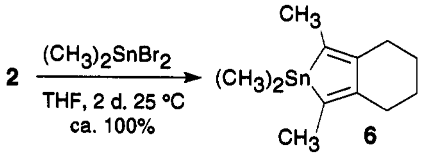
[23] See also: Fagan, P. J.; Nugent, W. A. *Org. Synth.* **1991**, *70*, 272–7.

[24] Ashe has reported that somewhat higher yields of **4b** can be obtained by iodinolysis of **1** followed by lithiation and transmetalation. See ref 5f.



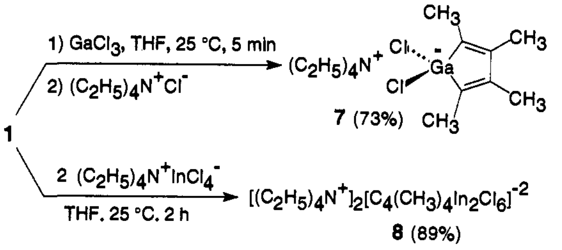
(4)

5a (E = Si, X = Br, ca. 28%)
5b (E = Ge. X = Cl. 83%)



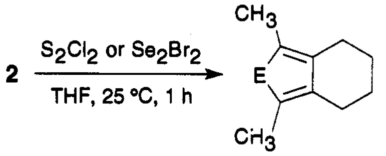
(5)

No reaction of **1** with $Et_4N^+GaCl_4^-$ was observed. However, reacting **1** with $GaCl_3$ in THF followed by addition of a dichloromethane solution of $Et_4N^+Cl^-$ allowed the isolation of gallole **7** (eq 6). The indium complex **8** was obtained by reaction of **1** with 2 equiv of $Et_4N^+InCl_4^-$ (eq 6). Heterole **8** precipitates from solution and can be recrystallized from dichloromethane ether. The structure of this compound has not been determined and is most likely a chloro-bridged indium dimer or higher oligomer.



(6)

The synthesis of sulfur- and selenium-containing analogues nicely demonstrates that the zirconacycle need not be isolated, and "one-pot" syntheses can be carried out. For example, zirconacycle **2** could be generated in situ in a manner analogous to eq 2 and then treated with 1 equiv of sulfur monochloride (eq 7). The thiophene **9a** was isolated in 55% yield after workup.[25]

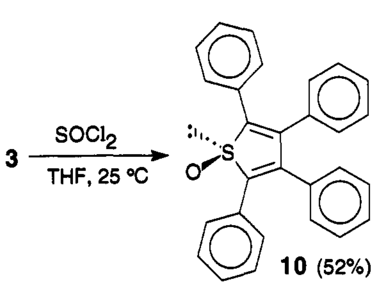


(7)

9a (E = S, 55%)
9b (E = Se, 53%)

In a similar manner, selenophene **9b** was obtained in 53% yield by reaction of **2** and Se_2Br_2 (eq 7). A rare example of a thiophene oxide (**10**) could be obtained by preparing **3** in situ and reacting it with thionyl chloride (eq 8).

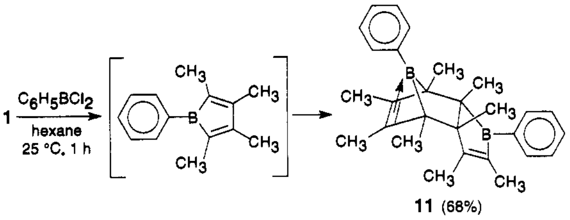
B. Synthesis of Borole Diels–Alder Dimers. Only one stable borole derivative is known, namely, pentaphenylborole, prepared independently by Eisch[10] and by Herberich.[14] Moreover, prior to our studies, the only known example of a borole Diels–Alder dimer was the dimer of 1-diisopropylamidoborole prepared by Herberich and co-workers through oxidation of the corresponding borole dianion with $SnCl_4$.[14] Therefore, we were pleased to discover that the metallacycle transfer strategy provides ready synthetic access to these interesting compounds.[9]



(8)

10 (52%)

Reaction of zirconium metallacycle **1** with phenylboron dichloride yields the Diels–Alder dimer of 1-phenyl-2,3,4,5-tetramethylborole (**11**), which can be isolated as a white solid in 68% isolated yield from cold (−78 °C) hexane (eq 9).



(9)

11 (68%)

As a solid, this compound is stable in air for at least 1 h but was generally handled under nitrogen. The compound is thermally stable even at elevated temperatures in solution. It will degrade upon storage at room temperature for several months, but storage at −20 °C in the solid state for at least 6 months did not lead to appreciable decomposition. Although 1-phenyl-2,3,4,5-tetramethylborole is presumably an intermediate in this reaction, it was not directly detected. We attempted to trap this intermediate by carrying out the reaction of the zirconium metallacycle with phenylboron dichloride in neat 2-butyne under dilute conditions at 25 °C and obtained an approximately 10% yield of 7-phenyl-1,2,3,4,5,6-hexamethyl-7-boranorbornadiene[9,26] under these conditions, with the rest of the product being **11**. This is evidence that the intermediate in this reaction is most likely the free borole since dimer **11** will not react with 2-butyne unless cracked by heating.[9] The low yield of trapping suggests that the borole has a greater propensity to undergo Diels–Alder reaction with itself than with 2-butyne.

As previously communicated, the structure of **11** was determined by an X-ray crystallographic investigation.[9] Two views of the structure are depicted in Figure 1. Tables 1 and 2 contain the bond lengths and bond angles determined for **11**.

A comparison of the bonding parameters found by Laube[17] for a 7-phenylnorbornenyl cation with those of **11** shows the close similarity between the two structures (Figure 1). These bonding parameters also correspond closely to those recently obtained from the theoretical calculations of Schulman et al.[27] The most notable feature of the structure is the bonding of the boron atom B1 to the carbon–carbon double bond C2–C3. The plane defined by C1, B1, and C4 makes an angle of 90.1° with the average mean plane defined by C1, C2, C3, and C4. The boron atom B1 is equidistant from C2 and C3 (1.864(7) Å). Note the boron atom remains sp^2 hybridized, with the phenyl group tipping only slightly away from the C2–C3 double bond (C11–B1–(midpoint C1,C4) = 1.5°).

We propose that the boron atom B1 and the carbons attached to it remain coplanar in order to maximize overlap of the empty boron p-orbital with the filled π orbital of the C2–C3 double bond. Tilting of the phenyl away from the C2–C3 bond would direct the empty orbital away from the π–electron density of the double bond. Tilting of the phenyl toward the C2–C3 bond might be favorable; however, the orbital extension of the lobe pointing

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(25) Buchwald has reported in ref 6c that higher yields of benzothiophenes can be obtained from the benzo-fused zirconacycles by treatment with sulfur dichloride rather than sulfur monochloride. In our studies on the non-benzo-fused zirconacycles to date, higher yields are obtained with S_2Cl_2 as compared with SCl_2. Similar observations have been made by others; see ref 6b and Tour, J. M. Personal communication.

(26) Fagan, P. J.; Nugent, W. A. Unpublished results.

(27) Schulman, J. M.; Disch, R. L.; von Ragué Schleyer, P.; Bühl, M.; Bremer, M.; Koch, W. *J. Am. Chem. Soc.* **1992**, *114*, 7897–901.

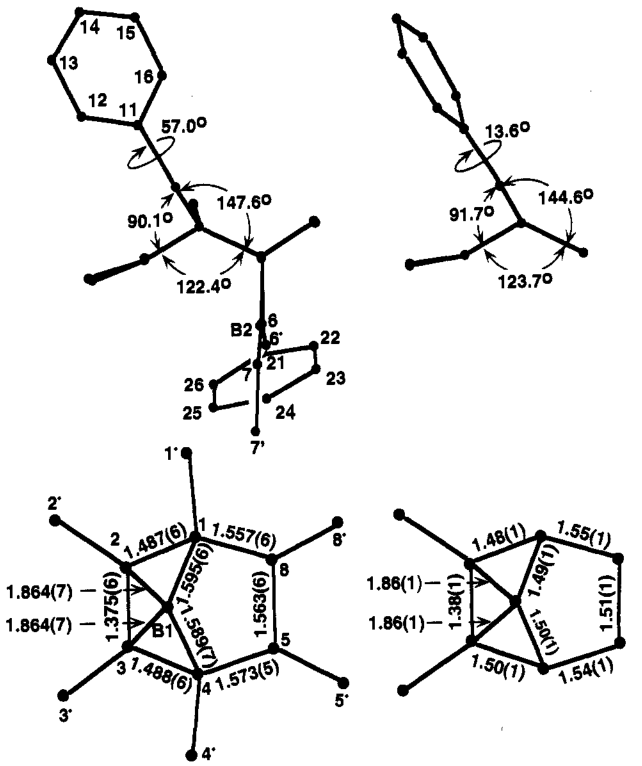


Figure 1. On the left, two views of **11** with only the carbon and boron atoms shown. An ORTEP drawing of **11** may be found in ref 9. On the right are the same two views of the structure of the 7-phenylnorbornenyl cation determined by Laube.[17]

Table 1. Interatomic Distances for **11** (Å)[a]

bond	distance	bond	distance
C(1)–C(1′)	1.520(6)	C(12)–C(13)	1.391(7)
C(1)–C(2)	1.487(6)	C(13)–C(14)	1.334(8)
C(1)–C(8)	1.557(6)	C(14)–C(15)	1.381(8)
C(2)–C(2′)	1.500(6)	C(15)–(16)	1.393(7)
C(2)–C(3)	1.375(6)	C(21)–C(22)	1.391(6)
C(3)–C(3′)	1.499(7)	C(21)–C(26)	1.394(6)
C(3)–C(4)	1.488(6)	C(22)–C(23)	1.380(6)
C(4)–C(4′)	1.532(6)	C(23)–C(24)	1.361(7)
C(4)–C(5)	1.573(5)	C(24)–C(25)	1.357(6)
C(5)–C(5′)	1.538(6)	C(25)–C(26)	1.386(6)
C(5)–C(6)	1.510(6)	C(1)–B(1)	1.595(6)
C(5)–C(8)	1.563(6)	C(2)–B(1)	1.864(7)
C(6)–C(6′)	1.502(7)	C(3)–B(1)	1.864(7)
C(6)–C(7)	1.361(6)	C(4)–B(1)	1.589(7)
C(7)–C(7′)	1.494(7)	C(7)–B(2)	1.520(7)
C(8)–C(8′)	1.528(6)	C(8)–B(2)	1.579(7)
C(11)–C(12)	1.402(6)	C(11)–B(1)	1.568(7)
C(11)–C(16)	1.373(7)	C(21)–B(2)	1.570(7)

[a] Numbers in parentheses are the estimated standard deviations.

Table 2. Intramolecular Angles for **11** (degrees)[a]

atoms	angle	atoms	angle
C(1′)–C(1)–C(2)	114.8(4)	C(21)–C(26)–C(25)	122.1(5)
C(1′)–C(1)–C(8)	116.9(4)	C(1′)–C(1)–B(1)	122.2(4)
C(2)–C(1)–C(8)	113.1(4)	C(2)–C(1)–B(1)	74.3(3)
C(1)–C(2)–C(2′)	124.6(5)	C(8)–C(1)–B(1)	108.4(3)
C(1)–C(2)–C(3)	110.6(4)	C(1)–C(2)–B(1)	55.5(3)
C(2′)–C(2)–C(3)	123.7(5)	C(2′)–C(2)–B(1)	136.3(4)
C(2)–C(3)–C(3′)	125.1(5)	C(3)–C(2)–B(1)	68.4(3)
C(2)–C(3)–C(4)	110.8(4)	C(2)–C(3)–B(1)	68.3(3)
C(3′)–C(3)–C(4)	123.4(5)	C(3′)–C(3)–B(1)	138.1(4)
C(3)–C(4)–C(4′)	115.3(4)	C(4)–C(3)–B(1)	55.2(3)
C(3)–C(4)–C(5)	112.1(4)	C(3)–C(4)–B(1)	74.5(3)
C(4′)–C(4)–C(5)	118.0(4)	C(4′)–C(4)–B(1)	120.9(4)
C(4)–C(5)–C(5′)	109.3(4)	C(5)–C(4)–B(1)	108.3(4)
C(4)–C(5)–C(6)	111.0(4)	C(6)–C(7)–B(2)	107.8(5)
C(4)–C(5)–C(8)	105.8(3)	C(7′)–C(7)–B(2)	128.1(5)
C(5′)–C(5)–C(6)	111.2(4)	C(1)–C(8)–B(2)	109.4(4)
C(5′)–C(5)–C(8)	114.4(4)	C(5)–C(8)–B(2)	103.7(4)
C(6)–C(5)–C(8)	105.0(4)	C(8′)–C(8)–B(2)	113.8(4)
C(5)–C(6)–C(6′)	121.0(4)	C(12)–C(11)–B(1)	123.2(5)
C(5)–C(6)–C(7)	115.0(4)	C(16)–C(11)–B(1)	120.4(4)
C(6′)–C(6)–C(7)	123.9(5)	C(22)–C(21)–B(2)	121.0(4)
C(6)–C(7)–C(7′)	123.8(5)	C(26)–C(21)–B(2)	123.0(4)
C(1)–C(8)–C(5)	106.2(3)	C(1)–B(1)–C(2)	50.2(3)
C(1)–C(8)–C(8′)	109.4(4)	C(1)–B(1)–C(3)	85.4(3)
C(5)–C(8)–C(8′)	114.0(4)	C(1)–B(1)–C(4)	99.3(4)
C(12)–C(11)–C(16)	116.5(5)	C(1)–B(1)–C(11)	129.6(4)
C(11)–C(12)–C(13)	120.2(6)	C(2)–B(1)–C(3)	43.3(2)
C(12)–C(13)–C(14)	121.2(6)	C(2)–B(1)–C(4)	85.7(3)
C(13)–C(14)–C(15)	121.2(5)	C(2)–B(1)–C(11)	124.2(4)
C(14)–C(15)–C(16)	117.4(6)	C(3)–B(1)–C(4)	50.3(3)
C(11)–C(16)–C(15)	123.6(5)	C(3)–B(1)–C(11)	125.2(4)
C(22)–C(21)–C(26)	116.0(4)	C(4)–B(1)–C(11)	131.2(4)
C(21)–C(22)–C(23)	121.5(5)	C(7)–B(2)–C(8)	108.1(4)
C(22)–C(23)–C(24)	120.7(5)	C(7)–B(2)–C(21)	125.8(5)
C(23)–C(24)–C(25)	119.9(5)	C(8)–B(2)–C(21)	126.1(5)
C(24)–C(25)–C(26)	119.8(5)		

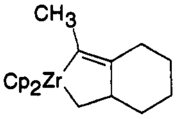
[a] Numbers in parentheses are the estimated standard deviations.

toward the π-electron density would decrease as the boron tends toward sp^3 hybridization. Indeed, the phenyl group does tip toward the carbon–carbon double bond in the 7-norbornenyl cation, but by only 4.4°.

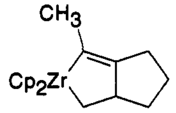
The methyl groups attached to the C2–C3 double bond are tilted up toward the phenyl group, and C2′ and C3′ are displaced out of the C1,C2,C3,C4 mean plane by 0.26 and 0.19 Å, respectively. This distortion was also noted in the 7-norbornenyl cation,[17] but is even more severe with the methyls displaced from the corresponding plane toward the phenyl group by 0.38 and 0.42 Å. We propose this distortion maximizes orbital overlap by tipping the carbon–carbon double-bond π-density toward the empty p-orbitals of the bridgehead atoms. Although this is a simplistic view, these features appear to be reproduced by theoretical calculations.[27]

The type of two-electron, three-centered bonding observed in **11** had originally been proposed by Winstein et al. for the isoelectronic 7-norbornenyl carbenium ions.[28] The isoelectronic situation in **11** was the first X-ray structural evidence that this was the case; the report of Laube subsequently confirmed this for the 7-phenylnorbornenyl cation.[17] With these results, the controversy regarding the ground-state bonding in these species can be put to rest.

C. Synthesis of 2,3- and 2,4-Dihydroheteroles. Treatment of enynes with low-valent metallocene equivalents is known to afford metallacyclopentene derivatives.[29] For purposes of our studies, the zirconacycles **12** and **13** were generated from 1-nonen-7-yne and 1-octen-6-yne, respectively. Again, the zirconacycles were cleanly generated from the enynes via treatment with zirconocene dichloride and *n*-butyllithium as originally described by Negishi.[19] Compounds **12** and **13** were not isolated but simply generated and utilized in situ.



12



13

Treatment of zirconacyclopentene **12** with sulfur monochloride afforded the dihydrothiophene **14** in 48% isolated yield (eq 10). Treating the same metallacycle with diphenyltin dichloride gave the corresponding stannacycle **15** (eq 10). The 2,3-dihydroselenophene ring system is rare, and no general synthetic route

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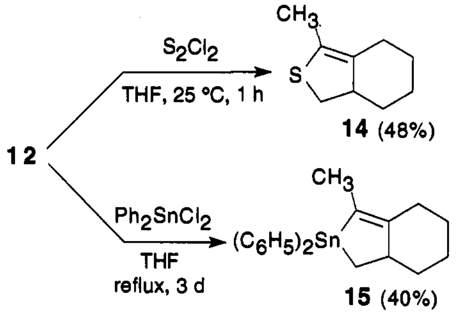
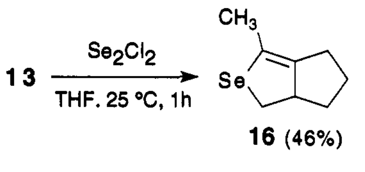
(28) Winstein, S. In Carbonium Ions; Olah, G. A., Schleyer, P. v. R., Eds.; John Wiley: New York, 1972; Vol. III, p 965 and references therein.

(29) (a) Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422–4. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568–9. (c) RajanBabu, T. V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128–35.

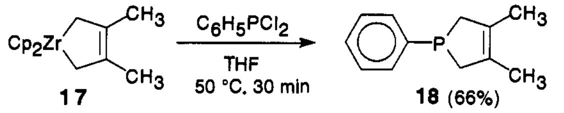


(10)

to these compounds had been reported prior to our studies.[30] Nevertheless, reaction of **13** with selenium(I) chloride was found to afford dihydroselenophene **16** in synthetically useful (46%) yield (eq 11). A single example[31] of a 2,4-dihydroheterole was also synthesized. The requisite metallacycle **17** was generated by *n*-butyllithium reduction of zirconocene dichloride in the presence of 2,3-dimethyl-1,3-butadiene.[19] Addition of 1 equiv of dichlorophenylphosphine afforded known phospholene **18**[32] in 66% yield (eq 12).

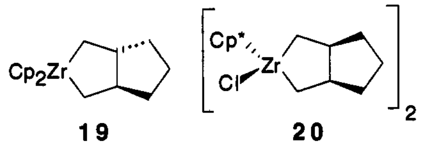


(11)

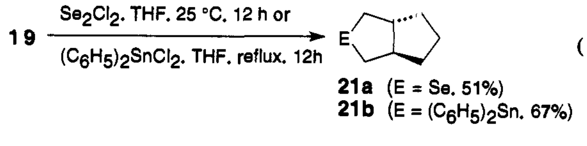


(12)

D. Synthesis of Tetrahydroheteroles. Both cis- and trans-fused zirconabicyclooctanes can be prepared by cyclizing a 1,6-diene with an appropriate zirconium reagent.[33] Thus, reduction of zirconocene dichloride with butyllithium in the presence of 1,6-heptadiene leads to the trans metallaindane **19**. In contrast, reduction of Cp*ZrCl$_3$[34] with sodium amalgam in the presence of the same diene gives cis metallaindane **20**.



Reaction of **19** with selenium(I) chloride in THF at room temperature afforded the trans-fused bicyclic selenide **21a** after flash chromatography on silica (eq 13). Reaction of **19** with diphenyltin dichloride was best carried out at reflux and afforded the trans-fused stannabicyclooctane **21b** (eq 13). In contrast, treatment of **20** in THF with Se$_2$Cl$_2$ or Ph$_2$SnCl$_2$ yielded the cis-fused analogues **22a** and **22b**, respectively.



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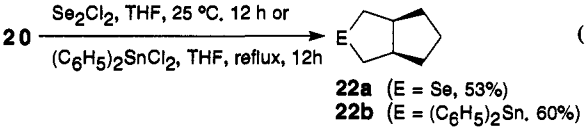
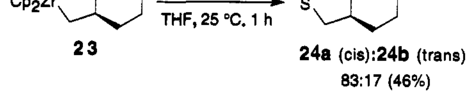
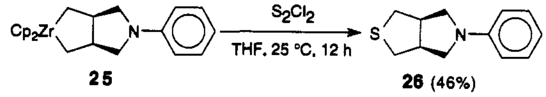


(14)

To gain further insight into the scope of this reaction, tetrahydrothiophenes **24** (83:17 mixture of cis and trans isomers) and **26** were also prepared (eq 15, eq 16). The requisite zirconacycles **23** and **25** were obtained by in situ reduction of zirconocene dichloride with butyllithium in the presence of 1,7-octadiene and *N,N*-diallylaniline,[35] respectively. Isolated yield for the mixture of **24a** (cis) and **24b** (trans) was 46%; **26** was isolated in 46% yield.

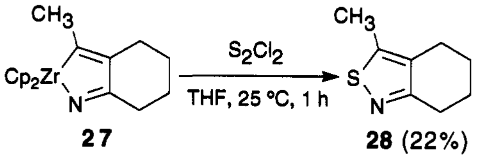


(15)



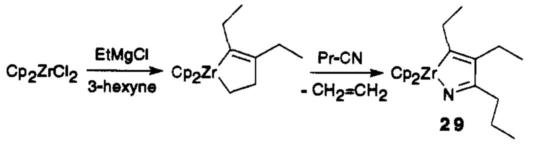
(16)

E. Synthesis of Isothiazoles. In an effort to extend this chemistry to the synthesis of heterocycles containing two heteroatom components, we have also briefly examined the synthesis of isothiazoles via metallacycle transfer.[18] The first approach we examined involved the azazirconacycle **27**. This complex was prepared by reducing zirconocene dichloride in the presence of bis(trimethylsilyl)acetylene followed by addition of 1-cyano-5-heptyne. (The bis(trimethylsilyl)acetylene stabilizes the low-valent zirconium reagent but is itself too hindered to undergo coupling reactions.) Reaction of **27** with sulfur monochloride (eq 17) afforded the desired isothiazole **28** after flash chromatography, but the result was not fully satisfactory. In particular, 67% of the starting 1-cyano-5-heptyne was recovered unreacted. The yield of **28** based on Cp$_2$ZrCl$_2$ was only 22%. (However, based on recovered nitrile the yield is 65%.)



(17)

Recently, a significant advance in the synthesis of azazirconacycles related to **28** has been reported by Takahashi, Negishi, and co-workers.[36] They discovered that acetylenes react with ethylmagnesium halides in the presence of zirconocene dichloride to afford the metallacyclopentene, as for 3-hexyne in eq 18.



(18)

Addition of a nitrile (as exemplified by butyronitrile in eq 18)

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[30] (a) Simple 2,3-dihydroselenophenes have been isolated from mixtures of hydrogen selenide and organic matter after heating to 300 °C in the presence of zeolites: Mamedov, E. Sh.; Babakhanov, R. A.; Akhverdieva, R. Ya.; Veinberg, A. K.; Mishiev, R. D.; Nasibov, Sh. S.; Lidak, M. Yu. *Khim. Geterosikl. Soedin.* **1986**, 1478–80. (b) See also: Konstantinova, T. G.; Gul'tyai, V. P.; Vitnivov, V. P.; Shteinshneider, A. Ya.; Daeva, E. D.; Moiseenkov, A. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1983**, 944–7.

[31] The arsenic analogue of **18** has also been prepared using an extension of our procedure; see ref 5c.

[32] Quin, L. D.; Mathewes, D. A. *J. Org. Chem.* **1964**, *29*, 836–9.

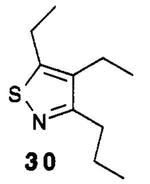
[33] (a) Nugent, W. A.; Taber, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 6435–7. (b) Rousset, C. J.; Swanson, D. R.; Lamaty, F.; Negishi, E. *Tetrahedron Lett.* **1989**, *30*, 5105–8.

[34] (a) Cp* = pentamethylcyclopentadienyl ligand: Blenkers, J.; de Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383–93. (b) Preliminary studies indicate that Cp*ZrCl$_3$ can be replaced with CpZrCl$_3$, which is available via an improved synthetic route: Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426–7.

[35] The stereochemistry of this cyclization using the biscyclopentadienyl reagent differs from other 1,6-dienes in that the predominant product is cis-fused; see ref 29a.

[36] Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687–90.

results in the loss of ethylene and concomitant formation of the azametallacycle **29**. This interesting new reaction should simplify access to isothiazoles via the metallacycle transfer reaction. In fact, generation of compound **29** in situ in this manner followed by addition of sulfur monochloride resulted in formation of isothiazole **30** in 51% isolated yield after chromatography. In a similar manner, isothiazole **31** was prepared from (trimethylsilyl)-propyne and benzonitrile. A small amount of a minor isomer with the trimethylsilyl and methyl groups transposed also forms in this reaction; the ratio of the major to minor isomer was 94:6. The regiochemistry of the major isomer **31** is tentatively assigned on the basis of an NOE study (vide infra).



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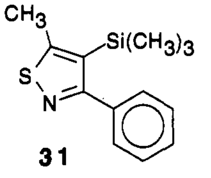


31

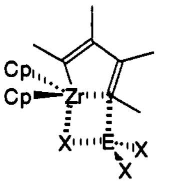
Discussion

The approach to heterocycle synthesis described above is conceptually related to the conversion of zirconacycles to carbocycles via carbonylation which was developed earlier by Negishi[37] and by Buchwald.[38] This approach typically involved treatment of a zirconacyclopentene derivative with carbon monoxide to afford a cyclopentenone. Rauchfuss[39] achieved similar transformations using $SCCl_2$. Phenyl isocyanide has also been utilized[40] as a carbon electrophile. A particularly visionary study was that of Whitesides and co-workers,[41] who as early as 1976 demonstrated that cis- and trans-bicyclic titanacyclopentanes could be carbonylated stereospecifically to yield the corresponding indan-2-ones.

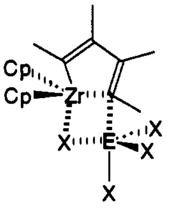
It is now evident that the metallacycle transfer approach can be applied to many types of heterocycles beyond the simple heteroles which first attracted our interest. Many other zirconium and related transition metal metallacycles are known,[42] and we expect the scope of this transformation to continue to expand. The range of elements that can be incorporated using the metallacycle transfer approach is also remarkable and already encompasses a wide swath of the main group elements. In addition, Dzemilev has provided evidence for metallacycle transfer from zirconium to aluminum.[43] It seems reasonable that this chemistry can be applied to heterocycles of tellurium and lead; however, a single experiment[26] with each of these metals did not afford discrete heterocyclic products. We should add that we did not optimize the yields of all reactions reported here; this should be possible with further effort. Our main purpose was to demonstrate the scope of this chemistry.

In our experience, the metallacycle transfer process is most efficacious for main group compounds which (1) can readily expand their coordination sphere from four to five coordinate, (2) are three coordinate, (3) are coordinatively unsaturated, or (4) are sterically unencumbered. In other words, compounds which can easily become hypervalent in transition states or in the ground state more readily accept the metallacycle from zirconium. For electronically satisfied compounds, it is well-known that this ability increases as one goes down a particular column of the main group elements (for the same oxidation state and coordination number). Thus, we were unable to achieve transfer of the metallacycle from **1** to silicon tetrachloride, and transfer proceeds slowly and in low yield for silicon tetrabromide. However for germanium tetrachloride, the reaction occurs nearly instantaneously and in high yield. Although four-coordinate silicon compounds can become five coordinate, tetrasubstituted germanium compounds do so much more readily. For group 13, a similar effect is observed: If one reacts $Et_4N^+GaCl_4^-$ with the zirconium metallacycle **1**, then no reaction takes place, even upon heating. However, $Et_4N^+InCl_4^-$ reacts with **1** within 2 h at room temperature to transfer the metallacycle from zirconium to indium. In contrast to $GaCl_4^-$, $GaCl_3$ which can become coordinatively unsaturated reacts rapidly.

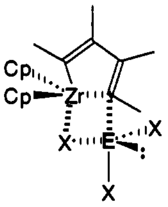
In general, three different transition states can be envisioned for the initial step in these metallacyle transfer reactions: **D** for a coordinatively unsaturated main group compound, **E** for a four-coordinate main group compound, and **F** for a three-coordinate compound with a lone pair. Clearly, steric interactions will be greatest for **E**, somewhat less for **F**, and even less for **D**. To some extent, this explains the relative reactivity observed for the main group compounds. It has been observed that substitution of chloride (X) with methyl retards the rate of transfer in reactions nominally with transition state **E**.[26]



D



E



F

The recent demonstration of selective C_β–$C_{\beta'}$ bond cleavage in zirconacyclopentenes by Takahashi, Negishi, and co-workers[36] has exciting implications for continued extensions of this chemistry. The particular application in eq 18 involves displacement of ethylene with a nitrile. However, alkynes and aldehydes were also shown to displace ethylene under comparable conditions; in some cases unsymmetrical alkynes could be added regioselectively.[36] This approach allows the synthesis of zirconacycles with unsymmetrical structures. More generally it expands the number of available zirconacycles for synthetic applications, including metallacycle transfer reactions.

Conclusion

The original heterole synthesis represented by eq 1 has now been substantially expanded. This current paper provides experimental details for the synthesis of some 29 different heterocycles incorporating a dozen different main group elements. The many important contributions of others which are cited throughout this paper have likewise greatly expanded the scope of this reaction. Continued exploration of this area should be fruitful.

Experimental Section

All procedures were carried out in a glovebox equipped with a constant nitrogen flush or in Schlenk-type glassware interfaced to a high-vacuum (10^{-4}–10^{-5} Torr) line. Diethyl ether, THF, hexane, and toluene were distilled from sodium/benzophenone under dinitrogen. The *n*-butyllithium solution was obtained from Foote Mineral Co. The molarity of this solution was determined by titration of 2.00 mL of the *n*-butyllithium solution in 10 mL of diethyl ether with dry 2-butanol using 1,10-phenanthroline as indicator. The reagents used in this study were purchased from commercial sources and purified, dried, and deoxygenated as necessary.

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(37) (a) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336–46. (b) See also refs 19 and 29b.

(38) Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113–4.

(39) Rauchfuss, T. B.; Bolinger, C. M. *Inorg. Chem.* **1982**, *21*, 3947–54.

(40) Davis, J. M.; Whitby, R. J.; Jaxa-Chamiec, A. *Tetrahedron Lett.* **1992**, *38*, 5655–8.

(41) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529–36.

(42) Review: Buchwald, S. L.; Nielson, R. B. *Chem. Rev.* **1988**, *88*, 1047–58.

(43) Dzhemilev, U. M.; Ibragimov, A. G.; Morozov, A. B.; Khalilov, L. M.; Muslukhov, R. R.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR. Ser. Khim.* **1991**, 1141–4.

Unless otherwise noted, flash chromatography was carried out on 230-400 mesh silica (EM Reagents) as described by Still.[44]

NMR spectra were recorded at 25 °C unless otherwise indicated. ^{13}C NMR spectra were recorded at a field strength of 75.5 MHz. ^{1}H NMR and ^{13}C NMR data are reported in parts per million downfield of TMS. ^{31}P NMR shifts are reported relative to external phosphoric acid (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad).

The determination of the X-ray structure of **11** was described previously.[9]

$Cp_2ZrC_4(CH_3)_4$ (1). A three-necked 500-mL round-bottomed flask was charged with Cp_2ZrCl_2 (27.03 g, 92.47 mmol), tetrahydrofuran (150 mL), and 2-butyne (16.0 mL, 204 mmol). The flask was cooled to −78 °C (dry-ice/ acetone bath), and then 1.72 M *n*-butyllithium (108 mL, 186 mmol) was added dropwise to the flask. After the addition was complete, the reaction mixture was stirred at −78 °C (dry-ice/acetone bath) for 10 min. The reaction mixture may become thick with a white solid at this point. The solid can be loosened by manually shaking the flask and with the aid of an external permanent magnet utilizing the magnetic stirring bar to break up the solid. (The solid loosens up some more upon warming, and stirring is not a problem.) The flask was then allowed to warm to room temperature by removing the dry-ice/acetone bath, and the reaction mixture was stirred for 2.5 h, at which point it was dark orange-red in color. Solvent was removed from the flask in vacuo. With the aid of a 40 °C water bath, the reaction residue was thoroughly dried. The flask was sealed and was brought into a nitrogen-filled glovebox. The residue was extracted with small portions of toluene (a total of 50 mL), and each portion was filtered and combined. Toluene was removed from this in vacuo. Hexane (20 mL) was added to the solid residue, and after trituration, the solid was collected by filtration and was washed once with hexane (10 mL). It was then dried in vacuo to yield 26.0 g (85%) of crystalline orange-red **1**. ^{1}H NMR (300 MHz, THF-d_8): δ 1.54 (s, 6 H, CH_3); 1.57 (s, 6 H, CH_3); 6.15 (s, 10 H, Cp).

1-Phenyl-2,3,4,5-tetramethylphosphole (4a). Procedure A. A 50-mL round-bottomed flask was charged with **1** (0.674 g, 2.04 mmol) and THF (10 mL). Following addition of dichlorophenylphosphine (277 μL, 2.11 mmol), the mixture was stirred for 1 h and solvent was removed in vacuo. The product was extracted from the residue with a total of 10 mL of hexane, and the extract was flash chromatographed on activity III alumina. The fractions containing product were combined, and solvent was removed in vacuo to yield **4a** (0.345 g, 78%) as a colorless liquid.

Procedure B.[23] A three-necked 500-mL round-bottomed flask equipped with a magnetic stirring bar, a rubber-septum-capped pressure-equalizing addition funnel on the center neck, a rubber septum on one side neck, and a stopcocked nitrogen inlet on the other side neck was charged with zirconocene dichloride (27.03 g, 92.47 mmol), tetrahydrofuran (150 mL), and 2-butyne (16.0 mL, 204 mmol). The flask was cooled to −78 °C (dry-ice/acetone bath), and 1.72 M *n*-butyllithium in hexane (108 mL, 186 mmol) was added dropwise to the stirred mixture in the flask. After addition was complete, the reaction mixture was stirred at −78 °C for 10 min. The flask was then allowed to warm to room temperature, and was stirred for 2.5 h, at which point it was dark orange-red in color. The flask was cooled again to −78 °C, and dichlorophenylphosphine (17.5 mL, 133 mmol) was added in a slow stream via syringe to the flask. The dry-ice/acetone bath was removed, and the flask was allowed to warm to room temperature. After 1 h the orange-red color had dissipated. Solvent was removed in vacuo. The reaction residue was extracted three times with 30-mL portions of hexane, each of which was filtered from the precipitate of Cp_2ZrCl_2 and combined. The hexane was removed in vacuo (0.5 Torr). Distillation at 0.35 Torr yielded a fraction which was collected between 40–92 °C, and this was discarded. A second fraction boiling between 92–104 °C was collected, and this clear oily liquid was identified as **4a** (16.1 g, 81% based on Cp_2ZrCl_2). The compound is air-sensitive and should be stored under nitrogen. ^{1}H NMR (300 MHz, THF-d_8): δ 1.89 (d, 6H, J_{PH} = 10.6 Hz, CH_3), 1.93 (s, 6H, CH_3), 7.24 (m, 5H, phenyl). ^{13}C NMR (THF-d_8): δ 12.9 (dq, J_{CH} = 126 Hz, J_{PC} = 22 Hz, CH_3), 13.9 (q, J_{CH} = 126 Hz, CH_3), 129.2 (dt, J_{CH} = 160 Hz and 6 Hz, J_{PC} = 8 Hz, phenyl), 129.6 (dt, J_{CH} = 162 and 6 Hz, para-CH), 134.3 (ddt, J_{CH} = 161, 5, and 5 Hz, J_{PC} = 20 Hz, phenyl), 134.7 (d, J_{PC} = 15 Hz), 136.4 (s), 143.4 (m, J_{PC} = 11 Hz). $^{31}P\{^1H\}$ NMR (121.7 MHz, THF-d_8, 25 °C): δ 14 (s). Exact mass. Calcd for $C_{14}H_{17}P$: *m/e* = 216.1068. Found: 216.1127.

1-Phenyl-2,3,4,5-tetramethylarsole (4b). A 100-mL round-bottomed flask was charged with **1** (0.600 g, 1.82 mmol) and THF (10 mL). After addition of phenyldichloroarsine (246 μL, 1.82 mmol), the reaction was stirred for 5 min, and solvent was then removed in vacuo. The product was extracted with a total of 5 mL of hexane, and the extract was subjected to flash chromatography on activity III alumina. The fractions containing product were combined, and solvent was removed in vacuo to yield **4b** (0.36 g, 78%). ^{1}H NMR (300 MHz, THF-d_8): δ 1.88 (s, 6H, CH_3), 1.96 (s, 6H, CH_3), 7.18–7.29 (m, 5H, phenyl). ^{13}C NMR (THF-d_8): δ 14.7 (q, J_{CH} = 126 Hz, CH_3), 14.9 (q, J_{CH} = 127 Hz, CH_3), 129.0 (dt, J_{CH} = 160 and 7 Hz, phenyl), 129.3 (dd, J_{CH} = 163 and 5 Hz, phenyl), 133.7 (dt, J_{CH} = 160 and 5 Hz, phenyl), 138.6 (s), 141.9 (s), 144.8 (s). Exact mass. Calcd for $C_{14}H_{17}As$: *m/e* = 260.0546. Found: 260.0552.

1-Phenyl-2,3,4,5-tetramethylstibole (4c). A 100-mL round-bottomed flask was charged with **1** (0.400 g, 1.21 mmol), $SbCl_3$ (0.277 g, 1.21 mmol), and THF (10 mL). After stirring for 2 min, 2.7 M phenyllithium in 30:70 ether/cyclohexane (470 μL, 1.27 mmol) was added. After 2 min, solvent was removed in vacuo, and the product was extracted with ca. 5 mL of hexane and was flash chromatographed on activity III alumina using hexane as eluant. The fractions containing the product were combined, and solvent was removed in vacuo to yield **4c** (0.290 g, 78%) as a colorless crystalline solid. ^{1}H NMR (300 MHz, THF-d_8): δ 1.87 (s, 6H, CH_3), 2.04 (s, 6H, CH_3), 7.20 (m, 3H, phenyl), 7.44 (m, 2H, phenyl). ^{13}C NMR (THF-d_8, −10 °C): δ 16.5 (q, J_{CH} = 126 Hz, CH_3), 18.2 (q, J_{CH} = 127 Hz, CH_3), 129.1 (dt, J_{CH} = 159 and 7 Hz, para-CH), 129.4 (dd, J_{CH} = 159 and 5 Hz, phenyl), 136.4 (dt, J_{CH} = 160 and 7 Hz, phenyl), 137.2 (s), 142.0 (s), 151.2 (s). Exact mass. Calcd for $C_{14}H_{17}Sb$: *m/e* = 306.0368. Found: 306.0354.

1-Phenyl-2,3,4,5-tetramethylbismole (4d). A 100-mL round-bottomed flask was charged with **1** (0.800 g, 2.43 mmol) and $BiCl_3$ (0.765 g, 2.43 mmol). After addition of THF (10 mL), the reaction mixture was stirred for 1 min and then phenyllithium (900 μL, 2.7 M in 30:70 ether/cyclohexane, 2.43 mmol) was added. After stirring for 2 min, solvent was then removed in vacuo. Product was sublimed (40 °C, 10^{-4}–10^{-5} Torr) from the reaction residue to yield pale yellow crystals of **4d** (0.66 g, 70% based on $BiCl_3$). The product can be further purified by an additional sublimation (40 °C, 10^{-4}–10^{-5} Torr). ^{1}H NMR (300 MHz, THF-d_8): δ 1.75 (s, 6H, CH_3), 2.29 (s, 6H, CH_3), 7.23 (m, 3H, phenyl), 7.87 (m, 2H, phenyl). ^{13}C NMR (THF-d_8, −10 °C): δ 20.5 (q, J_{CH} = 126 Hz, CH_3), 22.8 (q, J_{CH} = 126 Hz), 127.8 (dt, J_{CH} = 159 and 7 Hz, para-CH), 130.8 (dd, J_{CH} = 158 and 6 Hz, phenyl), 138.0 (dt, J_{CH} = 160 and 7 Hz, phenyl), 152.0 (br s, BiC), 159.2 (s), 160.7 (br s, BiC). Exact mass. Calcd for $C_{14}H_{17}Bi$: *m/e* = 394.1135. Found: 394.1110.

1,1-Dibromo-2,3,4,5-tetramethylsilole (5a). A 25-mL glass tube with a sealable Teflon stopcock was charged with **1** (5.00 g, 15.2 mmol) and freshly distilled $SiBr_4$ (5.00 mL, 40.3 mmol). The Teflon stopcock was sealed, and the flask was placed in an oil bath maintained at 150 °C **BEHIND A SAFETY SHIELD** such that the level of the oil was even with the level of the $SiBr_4$. After 47 h, the reaction tube was cooled, and the excess $SiBr_4$ was removed in vacuo. Hexane (20 mL) was added to the residue, and this was filtered. The solid residue was rinsed with small amounts of hexane, and these washings were combined with the filtrate. The filtrate was transferred to an oil sublimer, and excess hexane was removed in vacuo. The product was isolated by oil sublimation overnight at 90 °C, 10^{-4} Torr, as a colorless liquid. Yield: 1.24 g (ca. 28%). By ^{1}H NMR, product is primarily **5a** contaminated with ca. 9% of hexamethylbenzene. ^{1}H NMR (300 MHz, C_6D_6): δ 1.70 (s), 1.37 (s). ^{13}C NMR (THF-d_8): δ 11.0 (q, J_{CH} = 128 Hz), 14.2 (q, J_{CH} = 127 Hz) 125.3 (s), 151.4 (s).

1,1-Dichloro-2,3,4,5-tetramethylgermole (5b). A 25-mL flask was charged with **1** (0.600 g, 1.82 mmol) and THF (10 mL). After addition of $GeCl_4$ (400 μL, 3.51 mmol), the solution decolorized after 2 min and was stirred an additional 30 min when solvent was removed in vacuo. The product was extracted from the solid residue with a total of 25 mL of hexane, and this extract was then filtered. After removal of hexane from the filtrate in vacuo, sublimation of the residue yielded colorless crystalline **5b** (0.38 g, 83%). ^{1}H NMR (300 MHz, THF-d_8): δ 1.93 (s, 6H, CH_3), 1.95 (s, 6H, CH_3). ^{13}C NMR (THF-d_8): δ 12.7 (q, J_{CH} = 128 Hz, CH_3), 14.2 (q, J_{CH} = 127 Hz), 125.0 (s, C=C), 146.9 (s, C=C). Exact mass. Calcd for $C_8H_{12}Cl_2Ge$: *m/e* = 251.9527. Found: 251.9504.

Stannacyclopentadiene 6. A 25-mL round-bottomed flask was charged with **1** (1.00 g, 2.52 mmol), $(CH_3)_2SnBr_2$ (0.868 g, 2.81 mmol), and THF (10 mL). The reaction mixture was stirred for 48 h, at which time the color of the metallacycle had dissipated. Solvent was then removed in vacuo. The residue was extracted with hexane (5 mL) and was filtered. The solid residue on the glass frit was washed twice with 0.5-mL portions of hexane, and these washings were filtered and combined with the filtrate. Removal of solvent from the filtrate left 0.73 g (ca. 100%) of a pale orange liquid, which was essentially pure **6**. ^{1}H NMR (300 MHz, THF-

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[44] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–5.

d_8): δ 0.21 (s, 6H, satellites, $J_{SnH} = 55$ Hz, $SnCH_3$), 1.56 (m, 4H, CH_2), 1.90 (s, 6H, satellites, $J_{SnH} = 45$ Hz, CH_3), 2.36 (m, 4H, CH_2). ^{13}C NMR (THF-d_8): δ -10.5 (q, $J_{CH} = 130$ Hz, $J_{CSn} = 314$ and 300 Hz, $SnCH_3$), 18.2 (q $J_{CH} = 125$ Hz, satellites, $J_{CSn} = 62$ Hz, CH_3), 25.0 (t, $J_{CH} = 127$ Hz, CH_2), 28.7 (t, $J_{CH} = 125$ Hz, satellites, $J_{CSn} = 60$ Hz, CH_2), 149.3 (s, satellites, $J_{CSn} = 90$ Hz, $C{=}C$), 132.4 (s, satellites, $J_{CSn} = 38$ and 53 Hz, $C{=}C$). Exact mass. Calcd for $C_{12}H_{20}Sn$: m/e = 284.0587. Found: 284.0618.

$Et_4N^+(CH_3)_4C_4GaCl_2^-$ (7). A 25-mL flask was charged with **1** (0.300 g, 0.910 mmol), $GaCl_3$ (0.130 g, 0.738 mmol), and THF (10 mL). After stirring for 5 min, a solution of tetraethylammonium chloride (0.100 g, 0.603 mmol) in CH_2Cl_2 (10 mL) was added to the flask. After stirring for 30 min, the solution was filtered, and solvent was removed in vacuo. Then diethyl ether (10 mL) was added to the residue, and the solid was triturated and collected by filtration. The solid was washed three times with 30-mL portions of diethyl ether and was dried to yield 0.232 g of crude **7**. The crude product was recrystallized by dissolving in THF and filtering the resulting solution. Upon concentrating the THF in vacuo, a white solid precipitates, which was then collected by filtration, washed with ether, and dried in vacuo to yield **7** (0.150 g, 73%). ^1H NMR (300 MHz, CD_2Cl_2): δ 1.26 (tt, 12H, $J = 7.3$ and 1.5 Hz); 1.76 (s, 6H); 1.82 (s, 6H); 3.19 (q, 8H, $J = 7.3$ Hz). ^{13}C NMR (CD_2Cl_2): δ 7.8 (q, $J =$ 129 Hz); 14.0 (q, $J = 125$ Hz); 16.8 (q, $J = 124$ Hz); 52.9 (t, $J = 144$ Hz); 135.0 (s); 143.0 (s). Anal. Calcd for $C_{16}H_{32}Cl_2NGa$: C, 50.70; H, 8.51: N, 3.70; Cl, 18.71. Found: C, 50.59; H, 8.45; N, 3.60; Cl, 18.43.

$[(C_2H_5)_4N^+]_2[C_4(CH_3)_4In_2Cl_6]^{-2}$ (8). A 25-mL flask was charged with $Et_4N^+InCl_4^-$ (0.500 g, 1.29 mmol), **1** (0.212 g, 0.643 mmol), and THF (10 mL). After stirring for 2 h, a white precipitate was formed, and this was collected by filtration, washed twice with 10-mL portions of THF, and dried in vacuo to yield **8** (0.465 g, 89%). ^1H NMR (300 MHz, CD_2Cl_2): δ 1.32 (tt, 24H, $J_{HH} = 7.3$ Hz, $J_{NH} = 1.5$ Hz, CH_3CH_2N), 1.82 (s, 6H, CH_3), 1.91 (s, 6H, CH_3), 3.28 (q, 16H, $J_{HH} = 7.3$ Hz, CH_2N). ^{13}C NMR (CD_3CN): δ 7.7 (q, $J_{CH} = 128$ Hz, NCH_2CH_3), 16.3 (q, $J_{CH} = 126$ Hz, CH_3), 20.2 (q, $J_{CH} = 125$ Hz, CH_3), 53.0 (t, $J_{CH} = 144$ Hz, NCH_2), 148.5 (br s, $\mathrm{In}C{=}\mathrm{C}$), 156.0 (s, $\mathrm{InC}{=}C$). Anal. Calcd for $C_{24}H_{52}Cl_6N_2In_2$: C, 35.54; H, 6.46; N, 3.45; Cl, 26.23. Found: C, 35.31; H, 6.49; N, 3.38; Cl, 26.58.

Bicyclic Thiophene 9a. To a solution of zirconocene dichloride (2.34 g, 8.0 mmol) and 2,8-decadiyne (1.08 g, 8.0 mmol) in THF (100 mL) at −78 °C was added 1.6 M *n*-butyllithium in hexane (10 mL, 16 mmol). The solution was stirred for 1 h at room temperature, after which a solution of sulfur monochloride (1.08 g, mmol) in hexane (15 mL) was added. After an additional hour the reaction was quenched with 10% H_2SO_4, extracted with ether (3 × 100 mL), and dried ($MgSO_4$). Maleic anhydride (0.25 g) was added to remove any exocyclic diene present. The solvent was removed and the residue was purified by flash chromatography (hexane) to yield **9a** (0.73 g, 55%) as a pale yellow liquid. ^1H NMR (360 MHz, $CDCl_3$): δ 1.69 (m, 4H, CH_2), 2.23 (s, 6H, CH_3), 2.48 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.3, 23.1, 24.8, 127.3, 134.0. Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.49; S, 19.28. Found: C, 72.14; H, 8.49; S, 19.02.

Bicyclic Selenophene 9b. The procedure for **9a** was followed except that selenium(I) bromide (2.54 g, 8.0 mmol) was substituted for the S_2Cl_2; **9b** (0.90 g, 53%) was obtained as a pale yellow liquid: ^1H NMR (360 MHz, $CDCl_3$, 25 °C): δ 1.66 (m, 4H, CH_2), 2.13 (s, 6H, CH_3), 2.45 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.9, 23.3, 26.5, 133.2, 136.2. Exact mass. Calcd for $C_{10}H_{14}Se$: m/e = 214.0261. Found: 214.0267.

2,3,4,5-Tetraphenylthiophene Oxide (10). To a solution of zirconocene dichloride (1.17 g, 4.0 mmol) and diphenylacetylene (1.43 g, 8.0 mmol) in THF (50 mL) at −78 °C was added 1.6 M *n*-butyllithium in hexane (5.0 mL, 8.0 mmol). After stirring for 1 h at room temperature the mixture was cooled to 0 °C, and a solution of thionyl chloride (0.48 g, 4.0 mmol) in toluene (15 mL) was added dropwise. After the usual extractive workup (5% H_2SO_4, ether) and removal of solvent, the residue was triturated with hexane (50 mL) and the insoluble material was purified by flash chromatography (98:2 dichloromethane/ether) to afford **10** (0.84 g, 52%) as a bright yellow solid, which tenaciously retained 1 equiv of water as indicated by NMR. In order to obtain analytically pure **10** it was necessary to sublime the crude material in high vacuum (160 °C, 10^{-4} Torr). ^1H NMR (360 MHz, $CDCl_3$): δ 6.93 (m, 4 H), 7.1–7.3 (m, 16 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 128.05, 128.08, 128.45, 128.48, 129.57, 129.60, 130.38, 133.13, 140.92, 145.29. Anal. Calcd for $C_{28}H_{20}OS$: C, 83.14; H, 4.98; S, 7.93. Found: C, 83.16; H, 4.94; S, 7.86.

1-Phenyl-2,3,4,5-tetramethylborole dimer (11). A 300-mL round-bottomed flask was charged with **1** (20.00 g, 60.68 mmol) and hexane (200 mL). To this was added phenylboron dichloride (8.04 mL, 62.0 mmol). The solution became warm upon addition, and after stirring for 1 h, the hexane was filtered from precipitated Cp_2ZrCl_2. The Cp_2ZrCl_2 was washed twice with hexane (2-mL portions), and these washings were combined with the filtrate. Solvent was then removed from the filtrate in vacuo. The residue was extracted four times with 25-mL portions of hexane, and these were filtered and combined. Cooling to −78 °C and allowing the flask to stand for 2 h yielded a white precipitate, which was collected by cold (−78 °C) filtration. The solid was dried in vacuo to yield 8.15 g (68%) of **11**. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 0.76 (s, 3H, CH_3); 1.25 (s, 3H, CH_3); 1.27 (s, 3H, CH_3); 1.33 (s, 3H, CH_3); 1.59 (s, 3H, CH_3); 1.65 (s, 3H, CH_3); 1.82 (s, 3H, CH_3); 1.91 (s, 3H, CH_3); 7.08, 7.32, 7.43 (multiplets, 10H, phenyl). ^{13}C NMR (75.5 MHz, THF-d_8, 25 °C): δ 12.3 (q, $J_{CH} = 127$ Hz, CH_3); 12.8 (q, $J_{CH} = 127$ Hz, CH_3); 13.1 (q, $J_{CH} = 124$ Hz, CH_3); 13.3 (q, $J_{CH} = 125$ Hz, CH_3); 13.7 (q, $J_{CH} = 125$ Hz, CH_3); 15.2 (q, $J_{CH} = 125$ Hz, CH_3); 15.8 (q, $J_{CH} = 125$ Hz, CH_3); 19.7 (q, $J_{CH} = 126$ Hz, CH_3); 53.3 (br s, $\mathrm{B}C\mathrm{CH_3}$); 55.1 (br s, $\mathrm{B}C\mathrm{CH_3}$); 57.6 (br s, $\mathrm{B}C\mathrm{CH_3}$); 69.0 (s, $\mathrm{BC(CH_3){=}C(CH_3)}C$); 126.3 (s, $\mathrm{BC(CH3)}C{=}\mathrm{C}$); 127.2 (dt, $J_{CH} = 158$ and 6 Hz, phenyl); 128.0 (dt, 4C, $J_{CH} = 158$ and 5 Hz, phenyls); 129.0 (dt, $J_{CH} = 159$ and 7 Hz, phenyl); 129.8 ($\mathrm{BCC}{=}C$); 132.2 (dt, $J_{CH} = 157$ and 7 Hz, phenyl); 133.7 (dt, $J_{CH} = 156$ and 7 Hz, phenyl); 137.3 (v br s, BC(phenyl)); 141.8 (br s, BC(phenyl)); 144.1 (br q, $J_{CH} = 10$ Hz, $\mathrm{B}C{=}\mathrm{C}$); 183.7 (q, $J_{CH} = 5$ Hz, $\mathrm{BC}{=}C$). ^{11}B NMR (96.4 MHz, THF-d_8, 25 °C): δ −6.5, 70.0. Exact Mass. Calcd for $C_{28}H_{34}B_2$: m/e = 392.2846. Found: 392.2826. Anal. Calcd for $C_{28}H_{34}B_2$: C, 85.75; H, 8.74. Found: C, 85.86; H, 8.92.

Preparation of Dihydrothiophene (14). A 300-mL, round-bottomed flask with a septum-covered side arm was fitted with a septum-capped addition funnel having an N_2 inlet. The flask was charged with zirconocene dichloride (2.34 g, 8.0 mmol) and 1-nonen-7-yne (0.98 g, 8.0 mmol) in THF (100 mL). The addition funnel was charged with sulfur monochloride (1.08 g, 8.0 mmol) in hexane (15 mL). After flushing with nitrogen, the flask was cooled to −78 °C and 1.6 M butyllithium in hexane (10.0 mL, 16 mmol) was added via hypodermic syringe through the side arm. After 1 h the mixture was allowed to warm to room temperature and stirred an additional 1 h to generate **12**. The sulfur monochloride was then added, and after 1 h, the reaction was quenched with 10% sulfuric acid (100 mL) and extracted with ether (3 × 100 mL). The ether extracts were washed with saturated sodium bicarbonate and dried ($MgSO_4$), and the solvent was removed at reduced pressure. The residue was treated with trimethylphosphite (5 mL) to remove elemental sulfur, which tends to coelute with the product. Excess $P(OMe)_3$ was removed at reduced pressure, and the residue was purified by flash chromatography (85:15 hexane/toluene) to afford **14** (0.59 g, 48%) as a yellow liquid. ^1H NMR (360 MHz, $CDCl_3$): δ 1.4 (m, 3H), 1.60 (m, 1H), 1.70–1.82 (s overlapping m, 5H), 1.95 (m. 1H), 2.50 (d, 1 H, $J_{HH} = 15$ Hz), 2.75 (t, 1H, $J_{HH} =$ 10 Hz), 2.88 (m, 1H), 3.26 (dd, 1H, $J_{HH} = 11$ and 12 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.16, 25.33, 26.05, 27.00, 34.71, 36.15, 50.25, 124.43, 130.17. Exact mass. Calcd for $C_9H_{14}S$: m/e = 154.0816. Found: 154.0799.

Preparation of Stannacyclopentene 15. The previous procedure was followed except that dichlorodiphenyltin (2.75 g, 8 mmol) was used as electrophile and the mixture was heated for 3 days to ensure complete reaction. Flash chromatography (90:10 hexane/toluene) afforded **15** (1.25 g, 40%) as a viscous, colorless oil. ^1H NMR ($CDCl_3$): δ 0.75 (dd, 1H, $J_{HH} = 5$ and 14 Hz, $J_{SnH} = 46$ Hz), 0.9–1.9 (overlapping m's, 7H), 2.00 (s, 3H, CH_3), 2.05 (br m, 1H), 2.7–3.0 (m's, 2H). ^{13}C NMR ($CDCl_3$): δ 12.86 (^{119}Sn satellites $J_{SnC} = 353.84$ Hz), 17.99, 27.42, 28.04, 29.67, 40.83, 47.86, 127.24, 128.46 (meta), 128.49 (meta), 128.72 (para), 136.85 (ortho), 136.94 (ortho), 140.14, 140.42, 159.32. ^{119}Sn NMR ($CDCl_3$ versus tetramethyltin): δ 17.10. Anal. Calcd for $C_{21}H_{24}Sn$: C, 63.84; H, 6.12. Found: C, 64.12; H, 6.14. Exact mass. Calcd: 396.0900. Found: 396.0921.

Preparation of Dihydroselenophene 16. The procedure for **14** was followed substituting 1-octen-6-yne (0.87 g, 8 mmol) as the enyne component (generating **13**) and selenium monochloride (1.83 g, 8 mmol) as electrophile. Flash chromatography (90:10 hexane/toluene) afforded **16** (0.69 g, 46%) as an orange liquid. ^1H NMR (300 MHz, $CDCl_3$): δ 1.16–1.20 (m, 1H), 1.82–2.14 (overlapping m, 4H total) 1.89 (s with fine structure due to homoallylic coupling, 3H), 2.20 (br m, 1H), 3.04–3.20 (m, 2H), 3.43 (br m, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 16.86, 24.50, 30.56, 31.08, 32.12, 59.34, 118.20, 144.98. Exact mass. Calcd for $C_8H_{12}Se$: m/e = 188.0104. Found: 188.0919.

Preparation of Zirconacyclopentene 17.[19,45] A 500-mL three-necked round-bottomed flask was charged with Cp_2ZrCl_2 (20.29 g, 69.4 mmol), THF (200 mL), and 2,3-dimethyl-1,3-butadiene (8.30 mL, 73.4 mmol). The flask was cooled to -78 °C. Then *n*-butyllithium (1.60 M, 87.78 mL, 140 mmol) was added dropwise via an addition funnel. After the addition was complete, the reaction was stirred at −78 °C for another 5 min. It was then allowed to warm to room temperature and was stirred for 1.5 h. Solvent was removed in vacuo. Toluene was added to dissolve the product, and this was filtered. The residue on the frit was washed several times with toluene (a total of 325 mL) until all of the orange product was washed through the frit. The toluene was then removed in vacuo. A minimum of hexane was added to the residue, and after trituration the solid was collected by filtration. It was washed twice with a minimum of hexane (~10-mL portions) and dried in vacuo to yield 14.9 g (71%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.18 (br s, 4H, $ZrCH_2$), 1.75 (s, 6H, CH_3), 5.26 (s, 10H, C_5H_5).

1-Phenyl-3,4-dimethylphospholene (18). A 25-mL round-bottomed flask was charged with zirconacyclopentene **17** (0.800 g, 2.43 mmol) in THF (10 mL), and phenyldichlorophosphine (350 μL, 2.66 mmol). After stirring for 30 min at 50 °C, the solution had decolorized, and solvent was removed in vacuo. The product was extracted with hexane and purified by flash chromatography on activity III alumina using hexane as eluant. The fractions containing the product were combined, and hexane was removed in vacuo, yielding **18** as a colorless liquid (0.33 g, 66%). ^{1}H NMR (300 MHz, THF-d_8): δ 1.70 (s, 6H, CH_3), 2.47 (dq, 2H, J_{HH} = 16.4 and 3.3 HZ, C*H*H), 2.77 (dd, 2H, J_{HH} = 16 Hz, J_{HP} = 24.9 Hz, CH*H*), 7.23 (m, 3H, phenyl), 7.40 (m, 2H, phenyl). ^{13}C NMR (THF-d_8): δ 16.6 (q, J_{CH} = 125 Hz, CH_3), 41.1 (dt, J_{CH} = 131 Hz, J_{PC} = 12 Hz, CH_2), 128.9 (dm, J_{CH} = 160 Hz, phenyl), 129.0 (ddm, J_{CH} = 160 Hz, J_{PC} = 6 Hz, phenyl), 130.7 (d, J_{PC} = 3 Hz, C=C), 131.8 (ddt, J_{CH} = 159 and 7 Hz, J_{PC} = 19 Hz, phenyl), 143.8 (d, J_{PC} = 21 Hz, P*C*). ^{31}P{^{1}H} NMR (121.7 MHz, THF-d_8, 25 °C): δ −33 (s). Exact mass. Calcd for $C_{12}H_{15}P$: *m/e* = 190.0911. Found: 190.0970.

In Situ Generation of Zirconacycle 19. To a solution of 1,6-heptadiene (0.385 g, 4.0 mmol) and zirconocene dichloride (1.17 g, 4.0 mmol) in THF (50 mL) at −78 °C was added via syringe 1.6 M *n*-butyllithium in hexane (5.0 mL, 8.0 mmol). After 10 min the solution was allowed to warm to room temperature and stirring was continued for 2 h.

***trans*-2-Selenabicyclo[3.3.0]octane (21a).** To a solution of zirconacycle **19** generated as above was added selenium(I) chloride (0.92 g, 4.0 mmol), and the mixture was stirred at room temperature overnight. The solvent was removed at reduced pressure, and the residue was taken up in hexane (40 mL) and filtered. The product was isolated (0.36 g, 51%) by flash chromatography (90:10 hexane/benzene). ^{1}H NMR ($CDCl_3$): δ 1.25 (m, 2H), 1.71 (m, 2H), 2.22 (m, 4H), 2.47 (m, 2H), 2.88 (dd, *J* = 8 and 6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 24.04, 26.89, 30.50, 58.93. Anal. Calcd for $C_7H_{12}Se$: C, 48.01; H, 6.91. Found: C, 47.53, 47.59; H, 6.51, 6.37.

***trans*-2,2-Diphenyl-2-stannabicyclo[3.3.0]octane (21b).** To a solution of zirconacycle **19** generated as above was added diphenyltin dichloride (1.38 g, 4.0 mmol), and the mixture was heated at reflux overnight. The solvent was removed at reduced pressure, and the residue was taken up in hexane (40 mL) and filtered to remove coproduct Cp_2ZrCl_2. The crude product was isolated (0.99 g, 67%) by flash chromatography (90:10 hexane/toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.74 (t, *J* = 11 Hz, 2H), 1.21 (m, 2H), 1.52 (m, 2H), 1.66 (dd, *J* = 11 and 5 Hz, 2H), 1.90 (m, 4H), 7.35 (m, 6H), 7.54 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 15.32, 25.06, 33.06, 53.61, 128.42, 128.69, 136.62, 140.43. Anal. Calcd for $C_{19}H_{22}Sn$: C, 61.83; H, 6.01. Found: C, 61.71; H, 5.68.

In Situ Generation of Zirconacycle 20. To a solution of 1,6-heptadiene (385 mg, 4.0 mmol) and Cp^*ZrCl_3 (1.33 g, 4.0 mmol) in THF (50 mL) at -30 °C was added dropwise 0.5% sodium amalgam (40 g, 8.7 mmol). The mixture was stirred 2 h at −20 °C and 2 h at 0 °C.

***cis*-2-Selenabicyclo[3.3.0]octane (22a).** To a solution of zirconacycle **20** generated as above was added selenium(I) chloride (0.92 g, 4.0 mmol), and the mixture was stirred at room temperature overnight. The solvent was removed at reduced pressure, and the residue was taken up in hexane (40 mL) and filtered. The product was isolated (0.37 g, 53%) by chromatography (90:10 hexane/benzene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34–1.63 (m, 3H), 1.74–1.95 (m, 3H), 2.71 (m, 4H), 3.06 (m, 3.06). ^{13}C NMR ($CDCl_3$): δ 24.76, 30.39, 31.82, 50.64. Anal. Calcd for $C_7H_{12}Se$: C, 48.01; H, 6.91. Found: C, 48.11; H, 7.16.

***cis*-2,2-Diphenyl-2-stannabicyclo[3.3.0]octane (22b).** To a solution of zirconacycle **20** generated as above was added diphenyltin dichloride (1.38 g, 4.0 mmol), and the mixture was heated at reflux overnight. The solvent was removed at reduced pressure, and the residue was taken up in hexane (40 mL) and filtered to remove coproduct Cp_2ZrCl_2. The product was isolated (0.89 g, 60%) by flash chromatography (90:10 hexane/toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.04 (dd, *J* = 14 and 5 Hz, 2H), 1.33 (m, 4H), 1.53–1.95 (m, 4H), 2.48 (m, 2H), 7.33 (m, 6H), 7.57 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 13.38, 21.63, 32.54, 46.29, 128.36, 128.42, 128.60, 128.63, 136.68, 140.16. Anal. Calcd for $C_{19}H_{22}Sn$: C, 61.83; H, 6.01. Found: C, 61.69; H, 5.84.

Thiabicyclo[4.3.0]nonane (24). To a solution of 1,7-octadiene (441 mg, 4.0 mmol) and zirconocene dichloride (1.17 g, 4.0 mmol) in THF (50 mL) at −78 °C was added via syringe 1.6 M butyllithium in hexane (5.0 mL, 8.0 mmol). After 10 min the mixture was allowed to warm to room temperature and stirring was continued for 2 h. To this solution was added dropwise a solution of sulfur monochloride (0.54 g, 4.0 mmol) in toluene (10 mL), and the mixture was stirred 1 h. The reaction was quenched with 10% sulfuric acid (50 mL) and the product was extracted into ether (50 mL), was washed with aqueous sodium bicarbonate and then water, and was dried ($MgSO_4$). After distillation of the solvent the product was isolated (0.26 g, 46%) by flash chromatography (85:15 hexane/benzene). Gas chromatographic analysis indicated that the product was a mixture of cis isomer **24a** (83%) and trans isomer **24b** (17%). ^{1}H NMR (300 MHz, $CDCl_3$) **24a**: δ 2.88 (dd, 2H), 2.71 (dd, 2H), 2.28 (m, 2H), 1.57 (m, 6H), 1.38 (m, 2H). **24b**: 2.90 (m, overlap with **24a** resonance), 2.49 (t, 2H), 1.99 (dm, 2H), 1.76 (m, 2H); the remaining resonances for **24b** are obscured by those of **24a**. From a two-dimensional ^{1}H NMR/^{13}C NMR correlated spectrum, these remaining resonances are located at δ 1.58, 1.40, 1.24, and 1.06. ^{13}C NMR ($CDCl_3$) **24a**: δ 22.76, 26.09, 34.59 (SCH_2), 42.65 (methine). **24b**: δ 25.50, 31.27, 36.7 (SCH_2), 48.07 (methine). Anal. Calcd for $C_8H_{14}S$ (mixed isomers): C, 67.54; H, 9.92; S, 22.54. Found: C, 67.43; H, 9.54; S, 23.32. Exact mass. Calcd: *m/e* = 142.0817. Found: 142.0809.

***cis*-2-Phenyl-2-aza-6-thiabicyclo[3.3.0]octane (26).** To a solution of *N*,*N*-diallylaniline (0.69 g, 4.0 mmol) and zirconocene dichloride (1.17 g, 4.0 mmol) in THF (50 mL) was added 1.6 M butyllithium in hexane (5.0 mL, 8 mmol). After 10 min the solution was allowed to warm to room temperature and stirring was continued for 2 h to generate **25**. A solution of sulfur monochloride (0.54 g, 4.0 mmol) in toluene (10 mL) was added dropwise, and the mixture was stirred overnight. The reaction was quenched with saturated ammonium chloride (50 mL), and the product was extracted into ether (2 × 50 mL), washed with water (25 mL), and dried ($MgSO_4$). After removal of solvent at reduced pressure the residue was applied to the flash chromatography column with a little dichloromethane and eluted (90:10 hexane/ethyl acetate). Cuts 8–10 afforded a high-melting (156–157 °C) side product (0.07 g, 9%) tentatively identified as the trans isomer. The product **26** (0.38 g, 46%) was isolated from cuts 13–16 as a sharp-melting pale yellow solid, mp 61 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.78 (m, 2H), 3.04–3.22 (m, 6H), 3.54 (m, 2H), 6.57 (dd, *J* = 7 and 1 Hz, 2H), 6.68 (t, *J* = 8 Hz, 1H), 7.22 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 36.12, 47.31, 52.40, 112.03, 116.14, 129.08, 147.75. Anal. Calcd for $C_{12}H_{15}NS$: C, 70.20; H, 7.36; N, 6.82. Found: C, 69.20, 69.36; H, 7.28, 7.36; N, 6.67.

Bicyclic Isothiazole 28. In a nitrogen-filled glovebox, a flask was charged with excess magnesium turnings (1.43 g) and mercury(II) chloride (1.62 g) in THF (75 mL). After stirring 15 min, a solution of zirconocene dichloride (2.02 g, 6.9 mmol) and bis(trimethylsilyl)acetylene (1.42 g, 8.3 mmol) in THF (50 mL) was added dropwise. After an additional 4 h the mixture was filtered and 1-cyano-5-heptyne (0.84 g, 6.9 mmol) in THF (25 mL) was added dropwise. The reddish mixture turned yellow, and some solids separated. The mixture was stirred overnight, generating **27**, and then sulfur monochloride (0.93 g, mmol) in toluene (15 mL) was added dropwise. After 1 h the reaction was quenched with 5% H_2SO_4 and extracted into ether and the solvent removed. Flash chromatography in 80:20 hexane/ethyl acetate yielded, in addition to recovered 1-cyano-5-heptyne (0.56 g), isothiazole **28** (0.23 g, 22% yield, 65% yield based on recovered nitrile) as a pale yellow liquid. ^{1}H NMR (360 MHz, $CDCl_3$, 25 °C): δ 1.80 (m, 4H, CH_2), 2.37 (s, 3H, CH_3), 2.56 (m, 2H, CH_2), 2.82 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 11.20, 22.91, 22.96, 23.68, 29.73, 131.08, 156.17, 167.80. Exact mass. Calcd for $C_8H_{11}NS$: *m/e* = 153.0612. Found: 153.0608.

3-Propyl-4,5-diethylisothiazole (30). A solution of zirconocene dichloride (2.92, 10 mmol) and 3-hexyne (0.82 g, 10 mmol) in THF (100 mL) was cooled to −78 °C and 2.0 M ethylmagnesium chloride in ether (10 mL, 20 mmol) was added dropwise. The solution was then stirred 3 h at 0 °C, after which butyronitrile (0.69 g, 10 mmol) in THF (10 mL) was added via syringe. After 3 h at room temperature, sulfur monochloride

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(45) (a) Yasuda, H.; Kajihara, Y.; Mashima, K.; Lee, K.; Nakumura, A. *Organometallics* **1982**, *1*, 388 and references therein.

(1.35 g, 10 mmol) was added by syringe and stirring was continued overnight. The mixture was added to 5% H_2SO_4 (100 mL) and extracted into ether (3 × 100 mL). The ether phase was washed with saturated sodium bicarbonate (25 mL). After removal of solvent, the crude product was purified by flash chromatography (95:5 hexane/ether) to afford **30** as a pale yellow liquid (0.93 g, 51%). ^1H NMR ($CDCl_3$) δ 1.01 (t, J = 7 Hz, 3H), 1.10 (t, J = 7 Hz, 3H), 1.32 (t, J = 7 Hz, 3H), 1.79 (m, 2H), 2.54 (q, J = 7 Hz, 2H), 2.69 (dd, J = 6 and 7 Hz, 2H), 2.83 (q, J = 7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.3, 14.9, 15.5, 19.3, 20.6, 21.9, 34.0, 134.7, 184.6, 170.5. Exact mass. Calcd for $C_{10}H_{17}SN$: *m/e* 183.1082. Found: *m/e* 183.1090.

3-Phenyl-4-(trimethylsilyl)-5-methylisothiazole (31). A 2.0 M solution of ethylmagnesium chloride in ether (10.0 mL, 20 mmol) was added dropwise to a solution of zirconocene dichloride (2.92 g, 10 mmol) in THF (100 mL) at −78 °C. After 10 min a solution of 1-(trimethylsilyl)-1-propyne (1.12 g, 10 mmol) in THF (10 mL) was added via syringe. The bath was replaced with a 0 °C ice bath, and the mixture was stirred 3 h. A solution of benzonitrile (1.03 g, 10 mmol) in THF (10 mL) was added via syringe, and the mixture was stirred 3 h at room temperature. A solution of sulfur monochloride (1.35 g, 10 mmol) in hexane (10 mL) was added via syringe, and the mixture was allowed to stand overnight. Ether and saturated NH_4Cl (100 mL each) were added, and the mixture was stirred 15 min. The organic layer and additional ether extracts (2 × 100 mL) were dried ($MgSO_4$). The solvent was removed and the residue purified by flash chromatography (toluene then 95:5 toluene/ethyl acetate) to afford **31** as an amber liquid (0.69 g, 28%). Analysis by GC–MS (SP2100, 200 °C) indicated two products of *m/e* 247, with the larger peak at shorter retention time. The ratio of the major to minor isomer was 94:6, as determined by integration. For the major isomer: ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 2.66 (s, 3H), 7.38 (s, 5H). (Small singlets at δ 0.41 and 2.40 are tentatively assigned to the minor isomer.) ^{13}C NMR ($CDCl_3$): δ 0.95, 14.95, 128.06, 128.56, 129.05, 139.44, 170.79, 175.59. Exact mass. Calcd for $C_{13}H_{17}NSSi$: *m/e* 247.0851. Found: *m/e* 247.0855 (major isomer); 247.0623 (minor isomer). An NOE study indicated that irradiation of either the phenyl or methyl substituents in the major isomer resulted in a ca. 3% enhancement of the trimethylsilyl signal, while irradiation of the phenyl group had no effect on the methyl resonance.

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